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# COLLECTORLESS FLOTATION - BENEFICIATION OF CHALCOPYRITE AND SPHALERITE ORES

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# COLLECTORLESS FLOTATION - BENEFICIATION OF CHALCOPYRITE AND SPHALERITE ORES

by

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## ABSTRACT

The flotation recovery of chalcopyrite and sphalerite from copper, copper-zinc and lead-zinc-silver ores has been accomplished without using collectors. The ore samples are treated with sodium sulphide during wet-grinding with steel balls or during the conditioning period, which gives rise to the flotation of chalcopyrite with frother alone. Commercial grade copper concentrates have been produced without difficulty with recoveries comparable to, if not better than, those obtained by conventional modifier-collector-frother flotation. The zinc concentrates produced by activation of sphalerite with copper sulphate in the presence of sodium sulphide are also comparable to those obtained by conventional techniques, in terms of both grade and recovery. The collectorless flotation of chalcopyrite is best achieved at PH 6 and that of sphalerite is found to be improved significantly by aerative conditioning with sulphur dioxide. The use of frothers of high molecular weight, as well as hydrocarbon emulsions, is beneficial to the collectorless flotation. Good flotation of pyrite at alkaline pH has been achieved from the tailings of the collectorless flotation tests by using potassium amyl xanthate as a collector.

The form of natural floatability of chalcopyrite and activated sphalerite exhibited in the present work may be explained as being due to the incipient oxidation of the sulphide minerals induced by oxygen reduction, which may create a sulphur-rich surface, the sulphur being a hydrophobic entity. However, the possibility of clean sulphide minerals possessing inherent hydrophobicity in the absence of oxygen is not denied. The selectivity of a collectorless flotation process and the sphalerite activation mechanism have been explained on the basis of the differences in solubility products among sulphide minerals. Pyrite and pyrrhotite can also be activated by copper sulphate, which may be prevented, however, by aerative conditioning.

# INTRODUCTION

Sulphide minerals are readily amenable to flotation, but in most cases not without proper surface treatments. Thiol-type collectors are most widely used to render selected constituents of a sulphide ore hydrophobic. However, at the Tsumeb concentrator in South Africa galena and sphalerite are floated selectively from a chalcopyrite ore without using a collector in the first eight cells of each rougher bank (Boyce, et al 1970). Repetic (1974) has also shown that chalcopyrite can be floated successfully by using a frother alone after dry, autogenous grinding.

These recent reports on collectorless flotation have lead to a revival of the old controversy as to whether sulphide minerals are naturally hydrophobic or not (Finkelstein,et al 1975, Stewart and Finkelstein 1973, Fuerstenau 1975, Heyes and Trahar 1977). This issue of interest should be traced back to the days of oil flotation (Haynes 1860, Everson 1866) and skin flotation (Bradford 1865), which were essentially discovered from the fact that sulphide minerals are less wettable by water than silicious gangues. Since then, it was believed that many sulphide minerals were naturally hydrophobic, and Sulman (1930) and Gaudin (1932) noted that some sulphides such as galena and chalcopyrite were floatable without using a collector. Taggart et al (1934) and Wark (Ward 1938, Sutherland and Wark 1955a) opposed this view rather vigorously and contended that the apparent natural floatability was due to either contamination

or to the use of frothers which have collecting properties. They also believed that clean specimens became contaminated and gave finite contact angles if they were permitted to dry in air. Plaksin (1949) offered a different explanation, namely that the apparent hydrophobicity is due to the adsorption of molecular oxygen, which helps in promoting dehydration of sulphide minerals. Lepetic (1974) used this theory to explain the collectorless flotation of dry-ground chalcopyrite ore.

Ravitz and Porter (1933) were, on the other hand, in favour of the natural hydrophobicity theory, showing that galena cleaned of its surface oxidation products float completely with frother alone under oxygen free atmosphere. Fuerstenau (1975) also showed that clean samples of galena, pyrite and chalcopyrite float almost completely in the absence of oxygen, while the floatability of clean sphalerite is considerably less.

During the course of investigating the effect of surface oxidation of sulphide minerals on xanthate flotation, it was found that some minerals, notably chalcopyrite, float well in a microflotation cell without collector or frother, once the surface is cleaned of oxidation products. Consequently, it was decided to investigate if chalcopyrite in real ore samples could be made floatable by using sodium sulphide as a cleaning agent to remove the oxidation products. The use of the reagent as a promoter for a collectorless flotation has not been described in the literature, although it is frequently used to prepare clean surfaces of sulphide mineral specimens for the purpose of fundamental research. Encouraged by the initial test results

obtained with Robert Mine copper ore, described below, the work has been extended to the selective flotation of chalcopyrite and sphalerite from Texas gulf ores. Present work is an integral part of the CANMET's effort to develop new methods of achieving the maximum metallurgical recovery from Canadina complex zinc-lead-copper ores.

## EXPERIMENTAL

### A. Ore Samples

#### a) Robert Mine Copper Ores

The ore samples used in the present work were those left from a previous investigation, the results of which were reported by Raicevic and Bruce (1973). The samples had been crushed to -10 mesh after receipt on March 21, 1973 and stored in 2000g lots in our laboratory without any precautions to prevent possible surface oxidation of the sulphide minerals.

The ore contains 2.5% chalcopyrite, 20% pyrite, 50% quartz, 17% mica, 5% calcite, 4% kaolinized feldspar and 1% dolomite, the rest being comprised of sphalerite, galena, tetrahedrite, native silver and gold (Petruk, 1972). Table I gives the chemical analysis of the ore sample.

TABLE I: Head Sample Analysis of Robert Mine Copper Ore

| % Cu | % Pb | % Zn | oz/ton Au | oz/ton Ag |
|---|---|---|---|---|
| 1.0 | 0.02 | 0.06 | 0.44 | 1.9 |

b) Texasgulf Types 'A' and 'C' Ores

Two different ore samples were obtained from the Kidd Creek Mine, Texasgulf Canada Ltd.; a 100 pound sample of type 'A' ore was taken on December 21, 1976 and a 50 pound sample of type 'C' ore was taken on March 14, 1977 from the rod mill feeds. The samples received were crushed to all minus 10 or 20 mesh by passing through a gyratory crusher and a screen. They were riffled into 1000 g lots and stored in a freezer in order to minimize the possible oxidation of the sulphides. Representative head samples were analyzed for the metal values by the CANMET Chemical Laboratory as shown in Table II.

TABLE II: Head Sample Analysis of Texasgulf Type 'A' and 'B' Ores

| | % Cu | % Pb | % Zn | % Fe | oz/ton Ag |
|---|---|---|---|---|---|
| Type 'A' | 2.78 | 0.10 | 6.92 | 12.80 | 0.40 |
| Type 'C' | 0.37 | 0.74 | 10.12 | 20.40 | 6.15 |

Type 'A' ore is essentially a copper-zinc ore, while type 'C' ore is labelled as a lead-silver-zinc ore. The major metallic minerals are pyrite, sphalerite, chalcopyrite and galena, which are fine grained and complex in nature. Silver, more abundant in type 'C' ore, occurs principally as native grains with subordinate acanthite. The major gangue mineral is quartz, although chlorite, talc,pyrrhotite, siderite and cassiterite are present in small quantities.

B. General Experimental Procedure and Equipment.

A 1000g ore sample was ground in a porcelain laboratory ball mill (9" x 8 1/2") with 600 ml of tap water and 22 lbs of steel balls (5/8" to 7/8" diameter) for a desired period of time. The ground pulp was transferred into a rectangular rougher flotation cel (4.7ℓ capacity) made of stainless steel, and the cell was mounted on a Denver Sub-A laboratory flotation machine. After the remaining volume of the cell had been filled with tap water, appropriate reagents were added into the cell and the pulp was conditioned for a given period of time at 1,800 rpm prior to introducing air into the pulp to start the flotation. For cleaning operations either 2.5 or 1.25ℓ capacity flotation cells were used, depending on the volume of ore pulp to be treated, at impeller speeds of 1,200 or 800 rpm, respectively. For scavenger flotation, the rougher cell (4.7ℓ) was used at 1,800 rpm.

Each flotation product was analyzed for copper, lead and zinc by atomic absorption.

## RESULTS

A. Robert Mine Copper Ore.

In order to investigate the effect of sodium sulphide ($Na_2S$) on the collectorless flotation of chalcopyrite, varying amounts of $Na_2S$ (technical grade*) were added during the ball

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* Sodium sulphide flakes (Fisher Scientific Co.) were used, which contain 60-62% of $Na_2S$, more than 35% of water of crystallization, 1.5% of NaCl and 2% of unspecified other sodium salts.

mill grinding stages. A 25 minute grinding time was arbitrarily chosen for each test. The flotation feed thus produced was relatively coarse, 95.6% passing a 100 mesh screen. Each sample was conditioned for 10 minutes after the addition of Dow Froth 250 (0.088 lb/ton), and floated for 4 minutes in the rougher stage. The pH measured at the end of the conditioning period was found to increase with increasing amount of $Na_2S$ added; it varied from pH 8.27 at the 0.38 lb/ton $Na_2S$ addition to pH 10.48 at 3.76 lb/ton. It may be noteworthy that the pH dropped

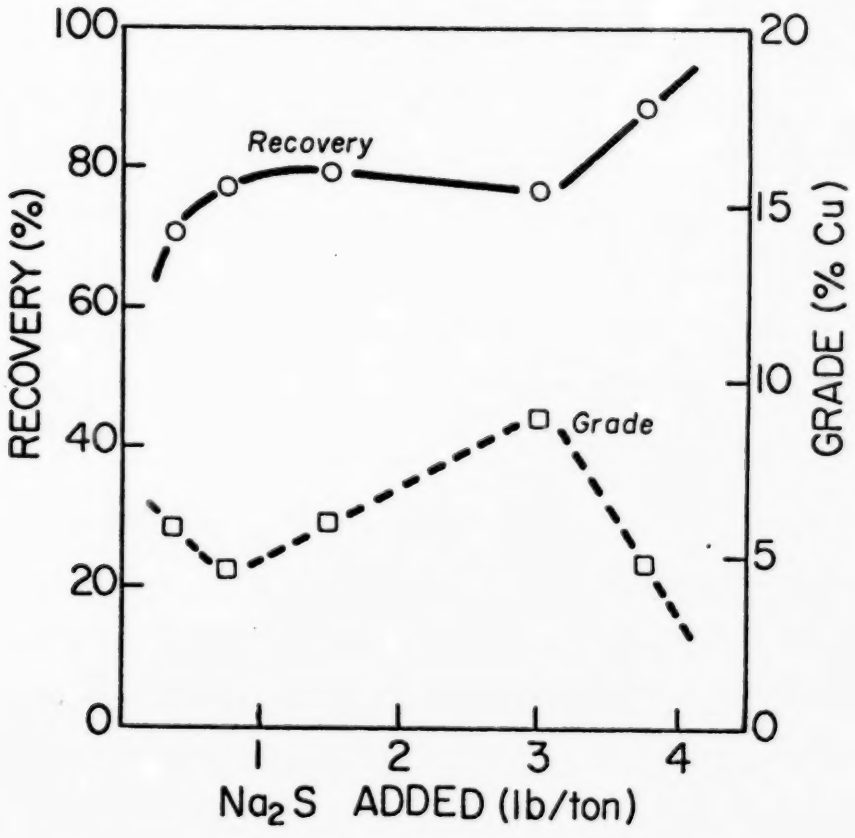


Fig. 1. Effect of sodium sulphide on the collectorless flotation of Robert Mine copper ore.

considerably at the end of the 4 minute rougher flotation, which may indicate some sort of oxidation. The rougher flotation was immediately followed by one cleaning operation, which took about 3 to 4 minutes to obtain barren froth. No reagents were added during cleaning.

Fig. 1 represents the flotation test results obtained with the Robert Mine copper ore. It shows that chalcopyrite is floatable without using a collector if the surface is cleaned of its oxidation products by $Na_2S$. Under the present experimental conditions, the grade of the copper concentrate reached a maximum of 8.8% Cu with the recovery of 76.8% when 3 lb/ton of $Na_2S$ was used. The low grades of the concentrates are largely due to the relatively coarse grind, but considerable quantity of free pyrite grains floated with the chalcopyrite particularly when more than 3 lb/ton of $Na_2S$ was used. It appears, nevertheless, that $Na_2S$ reacts with chalcopyrite in preference to pyrite, considering that the ore contains 20% of pyrite and only 2.5% of chalcopyrite.

The selectivity of collectorless flotation using $Na_2S$ as a cleaning agent was found to be improved (significantly) by lowering the pH of the pulp after the sulphidization: The natural pH of the ore pulp, ground for 25 minutes with 3.76 lb/ton of $Na_2S$, was 10.5. The pH was brought down to 6.0 by adding hydrochloric acid to the flotation cell and the pulp was conditioned for 30 minutes prior to the flotation. The ore was floated for 3 minutes in the rougher stage using 0.08 lb/ton of DF 250, and cleaned once until exhaustion. It was necessary

to add 0.04 lb/ton of DF 250 for cleaning, since the froth was brittle, unlike those tests made at natural pH's. The result of the test work is given in Table III, showing that the simple collectorless flotation technique can be used to produce a commercial grade copper concentrate with acceptable

TABLE III: Collectorless Flotation of Robert Mine Copper Ore at pH 6.0 by using 3.76 lb/ton of $Na_2S$

| Products | Weight (%) | Assay (% Cu) | Distribution (%) |
|---|---|---|---|
| Concentrate | 2.58 | 21.35 | 68.08 |
| Cleaner Tail | 2.39 | 3.65 | 10.78 |
| Tail | 95.03 | 0.18 | 21.15 |
| Feed | 100.00 | 0.81 | 100.00 |

recovery. The results given in Table III are in fact superior to those obtained by using the conventional modifier-collector-frother flotation technique: Raicevic and Bruce (1973) obtained 20.0% copper concentrate with only 38.7% recovery from the same ore ground to all -100 mesh. They used lime as a pyrite depressant, potassium amylxanthate as a collector and pine oil as a frother. The collectorless flotation technique developed in the present work should produce even better results than those shown in Table III if a finer grind to improve the liberation is incorporated.

B. Texasgulf Type 'A' Ore

a) Flotation of Chalcopyrite Ore

Two preliminary flotation tests were conducted in parallel with the Texasgulf Type 'A' ore: In Test TA-1, the ore (minus 10 mesh) was ground for 20 minutes in the presence of 1.67 lb/ton of $Na_2S$ and floated at the natural pH (=8.8) by using 0.08 lb/ton of DF 250. The rougher concentrate was cleaned once without any further reagent addition. In Test TA-2 the pH of the ore pulp, ground under the identical conditions to those of TA-1, was adjusted to 6.0 by HCl and floated in the same manner. The results of the two tests are given in Table IV, showing that a higher grade copper concentrate was obtained when the pH was lowered after the sulphidization. This confirms the results obtained with Robert Mine copper ore described in the foregoing section. Table IV also shows that sphalerite is not activated by $Na_2S$ alone, which is a significant indication that the collectorless flotation could be used for the differential flotation of a copper-zinc ore.

b) Differential Flotation of Chalcopyrite and Sphalerite

*a. With coarse grinding*

A preliminary test was made to float sphalerite from a copper rougher tailing by activating it with copper sulphate ($CuSO_4.5H_2O$). Fig. 2 represents the laboratory flowsheet and the reagent balance of the collectorless flotation test (TA-3). The ore was ground for 20 minutes, the first five minutes with HCl and the remaining 15 minutes with $Na_2S$. The pH of the pulp diluted to the volume of rougher flotation cell was 6.6.

TABLE IV: Flotation of Chalcopyrite from Texasgulf Type 'A' Ore at pH 8.8 and 6.0

| Test No. and Remarks | Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TA-1<br>20' grind, 1.67 lb/ton $Na_2S$, 0.08 lb/ton DF-250, and floated at pH 8.8 (natural). | Cu conc | 11.90 | 18.65 | 0.26 | 9.64 | 85.44 | 27.49 | 16.82 |
| | Cu cl tail | 2.71 | 0.72 | 0.17 | 9.64 | 0.75 | 4.09 | 3.83 |
| | tail | 85.39 | 0.42 | 0.09 | 6.34 | 13.81 | 68.42 | 79.36 |
| | Feed | 100.00 | 2.60 | 0.11 | 6.82 | 100.00 | 100.00 | 100.00 |
| | Cu ro conc | 14.61 | 15.32 | 0.24 | 9.64 | 86.19 | 31.58 | 20.65 |
| Test TA-2<br>20' grind, 1.67 lb/ton $Na_2S$, 0.08 lb/ton DF-250, and floated at pH 6.0 by adding HCl. | Cu conc | 10.40 | 21.57 | 0.38 | 9.26 | 86.73 | 41.49 | 14.54 |
| | Cu cl tail | 2.13 | 0.92 | 0.15 | 11.81 | 0.76 | 3.36 | 3.19 |
| | tail | 87.47 | 0.37 | 0.06 | 6.23 | 12.51 | 55.15 | 82.27 |
| | Feed | 100.00 | 2.59 | 0.10 | 6.62 | 100.00 | 100.00 | 100.00 |
| | Cu ro conc | 12.53 | 18.06 | 0.34 | 9.37 | 87.49 | 44.85 | 17.73 |

Chalcopyrite was first floated by adding DF250 and the rougher concentrate was cleaned once. For sphalerite flotation, $Na_2S$, $CuSO_4$ and DF1400 were added to the copper rougher tailing, which was followed by a 10 minute conditioning period. The rougher flotation was made at the natural pH and the concentrate was cleaned once. Each flotation in test TA-3 was performed until exhaustion.

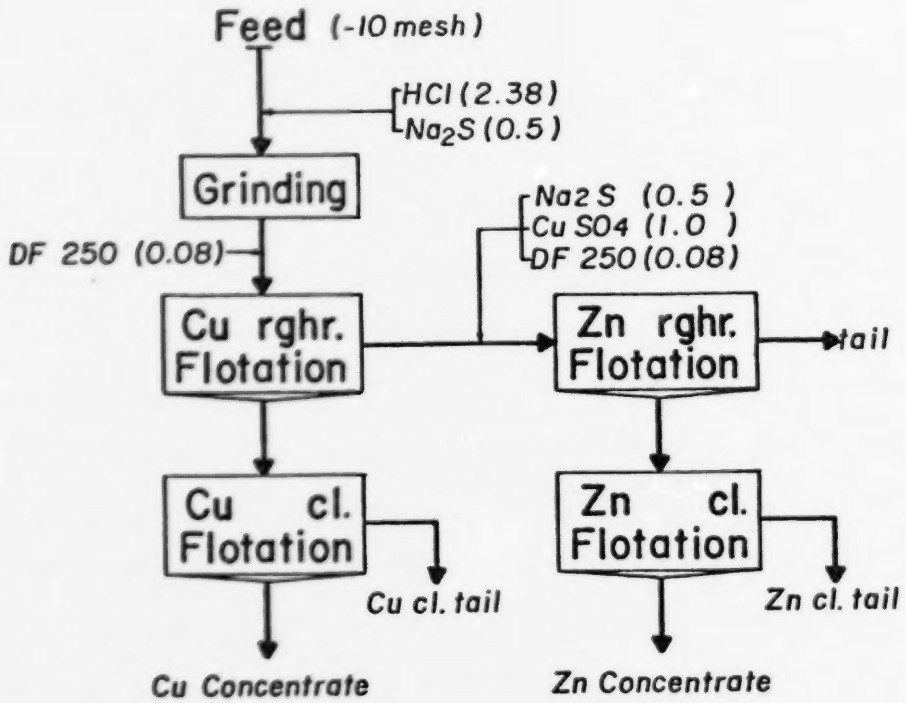


Fig. 2. Laboratory flowsheet and reagent balances of test TA-3. The numericals represent the reagent addition in pounds per ton of ore feed.

TABLE V: Results of Test TA-3

| Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|
| | | Cu | Pb | Zn | Cu | Pb | Zn |
| Cu conc | 11.45 | 20.45 | 0.42 | 8.56 | 89.23 | 49.59 | 14.47 |
| Cu cl tail | 1.99 | 1.60 | 0.16 | 18.62 | 1.21 | 3.30 | 5.47 |
| Zn conc | 5.04 | 0.41 | 0.09 | 56.63 | 0.79 | 4.64 | 42.14 |
| Zn cl tail | 0.56 | 0.72 | 0.13 | 12.04 | 0.15 | 0.72 | 0.99 |
| Tailings | 80.96 | 0.28 | 0.05 | 3.09 | 8.62 | 41.75 | 36.93 |
| Feed | 100.00 | 2.63 | 0.10 | 6.77 | 100.00 | 100.00 | 100.00 |

The results given in Table V, show that a commercial grade copper concentrate assaying 20.45% Cu was obtained with a satisfactory recovery of 89.23%. A high grade zinc concentrate assaying 56.63% Zn was produced, but the recovery was only 42.14%. The poor zinc recovery was undoubtedly due to the incomplete liberation of the sphalerite grains from pyrite. Note, here, that the final copper concentrate assays 8.56% Zn, which amounts to 14.5% of the total zinc content. Attempts were made, therefore, made to suppress sphalerite during the copper rougher flotation by using various depressants such as zinc sulphate, sodium cyanide, sodium bisulphite and potassium permanganate, but without success. The failure of the sphalerite suppression was not because the depressants used in the present work were ineffectual, but was more likely due to incomplete liberation of sphalerite from pyrite grains. It was found from other tests that sphalerite was completely suppressed by these depressants when they are added to a

zinc rougher or a cleaner flotation cell in sufficient quantities. The sphalerite can be reactivated, however, by the fresh addition of $Na_2S$ and $CuSO_4$.

*b. With Regrinding*

Based on the information obtained from Test TA-3, efforts were made to improve the zinc recovery by regrinding both the copper rougher concentrate and tailing for various lengths of time. Figs. 3 and 4 represent the laboratory flowsheets and the reagent balances of tests TA-4 and TA-5, respectively. In both tests the ore feed (-10 mesh) was ground for 25 minutes, and the copper tails were reground for 20 minutes. The regrinding was done with one half of steel ball charge. The major differences of the two tests are that in test TA-4 the copper rougher concentrate, combined with the copper scavenger concentrate, was reground for 30 minutes without reagent addition prior to the two cleaners, while in Test TA-5 it was reground for 50 minutes with 0.5 lb/ton of $Na_2S$ prior to the three cleaners. The reagent balances used in other parts of the copper-zinc flotation circuits were, however, kept identical in the two tests. DF 1400 was used, since it appeared to be more beneficial to zinc flotation than DF 250. The zinc rougher flotation is shown in the flowsheets as a single stage operation, but it was actually conducted in two stages; first with 0.5 lb/ton of $Na_2S$ and 2.0 lb/ton of $CuSO_4$ and then 0.5 lb/ton of $Na_2S$ and 0.6 lb/ton of $CuSO_4$, each followed by a 15 minute conditioning period. The frother was added at

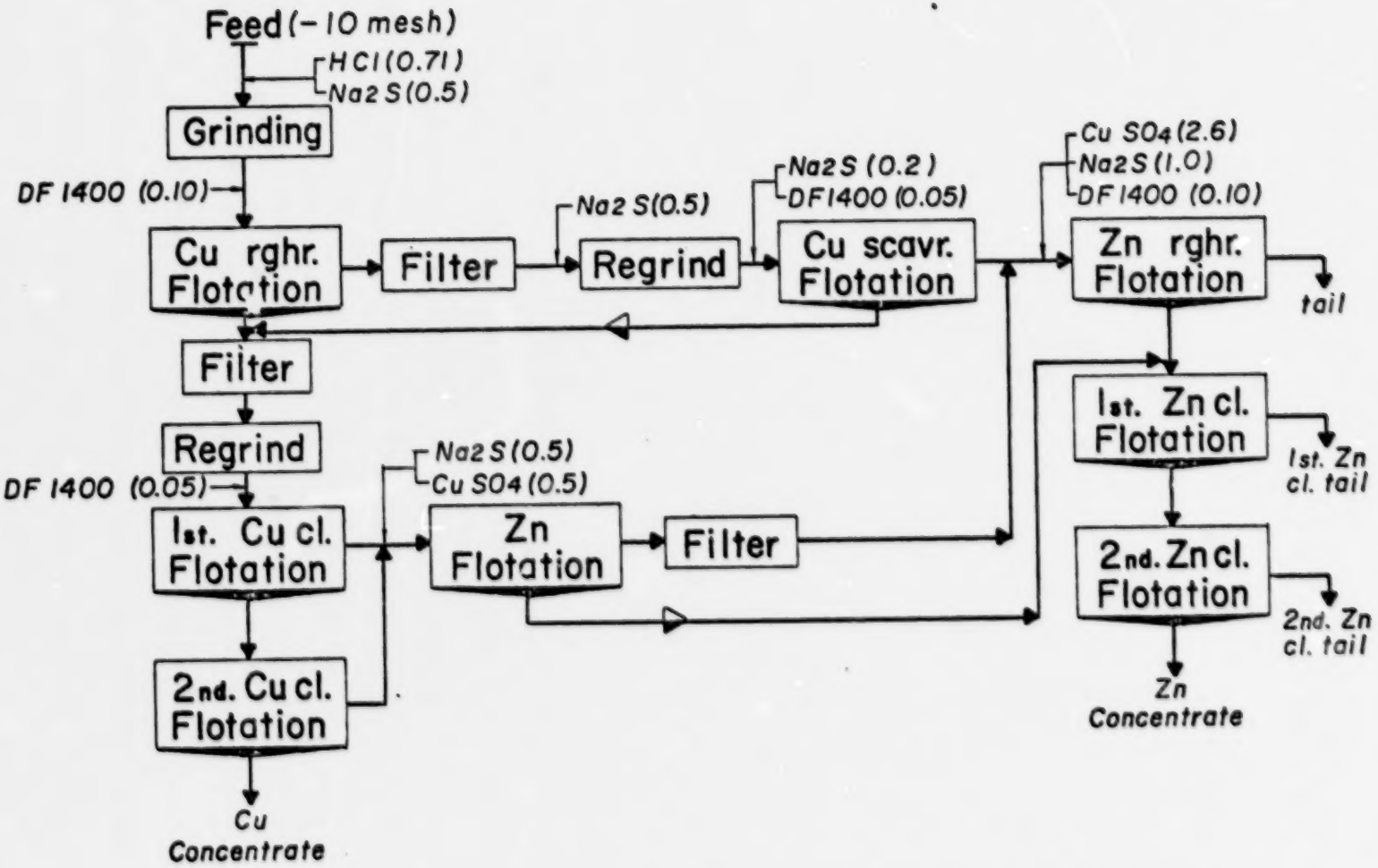


Fig. 3. Laboratory flowsheet and reagent balance (lb/ton) of test TA-4.

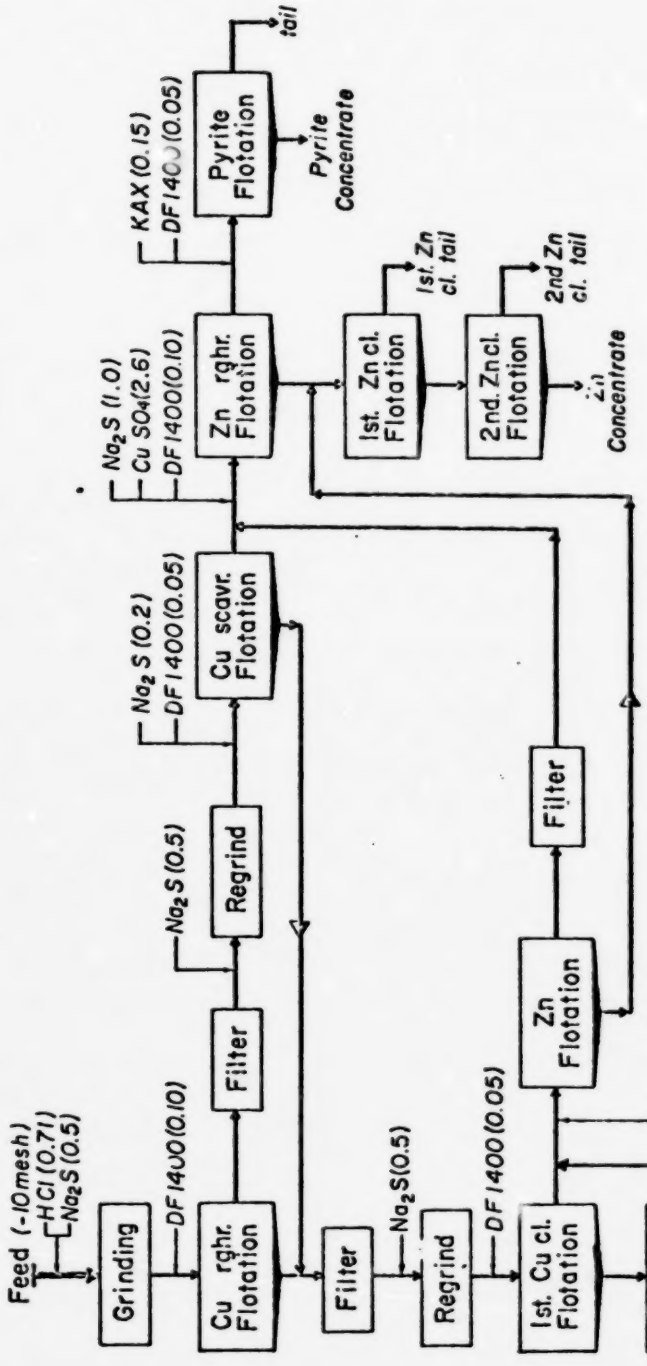


Fig. 4. Laboratory flowsheet and reagent balance (lb/ton) of test TA-5.

the 10 minute mark of each conditioning period. The flotation was conducted until exhaustion, which took a total of 8 minutes in the zinc rougher and 3½ minutes in the copper rougher. The pH's of the copper and zinc rougher flotation were 7.6 and 9.5, respectively, as measured prior to the flotation.

A rather interesting observation was made in Test TA-5 when potassium amylxanthate (KAX) was added to the zinc rougher tail in an attempt to see if any recoverable sphalerite was left after the collectorless flotation. It was found, instead, that pyrite was floating rather vigorously with the first dosage (0.05 lb/ton) of KAX. Most of the pyrite seemed to have floated after two more successive additions of KAX. Pyrite does not readily float under alkaline conditions using KAX (Gaudin, 1957), but it was made floatable in the presence of $Na_2S$. The pH of the pulp measured at the end of pyrite flotation was 9.0.

The results of test TA-4 and TA-5 are given in Table VI. One can see that much improved zinc recoveries were obtained as a result of regrinds, although the grades of the final zinc concentrates were considerably lower than that obtained with the coarser grind (Test TA-3, Table V). Note also that the copper concentrate of Test TA-5 has a substantially lower zinc assay (6.95% Zn) than that of Test TA-4 (10.21% Zn), which is most likely due to the longer regrind of the copper rougher concentrate. The copper concentrates of both tests are of about the same grade but the recovery drops with the longer regrind of the copper rougher concentrate despite the fact that the tails show lower

TABLE VI: Results of Tests TA-4 and TA-5

| Test No. and Remarks | Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| **Test TA-4** | | | | | | | | |
| 30 minute regrind of Cu rghr. conc with no reagents prior to two Cu cleaners. | Cu conc | 10.59 | 22.89 | 0.42 | 10.21 | 87.27 | 43.58 | 16.01 |
| | Zn conc | 12.59 | 1.02 | 0.16 | 40.26 | 4.62 | 19.69 | 75.06 |
| | 1st Zn cl tail | 7.24 | 1.06 | 0.11 | 2.65 | 2.76 | 7.84 | 2.84 |
| | 2nd Zn cl tail | 1.22 | 2.09 | 0.18 | 5.70 | 0.92 | 2.15 | 1.03 |
| | Tail | 68.36 | 0.18 | 0.04 | 0.50 | 4.43 | 26.74 | 5.06 |
| | Feed | 100.00 | 2.78 | 0.01 | 6.75 | 100.00 | 100.00 | 100.00 |
| **Test TA-5** | | | | | | | | |
| 50 minute regrind of Cu rghr. conc with 0.5 lb/ton of $Na_2S$ prior to three Cu cleaners. Pyrite flotation by KAX from Zn rghr. tail. | Cu conc | 9.39 | 23.57 | 0.47 | 6.95 | 82.73 | 43.32 | 9.74 |
| | Zn conc | 11.51 | 1.71 | 0.13 | 43.41 | 7.36 | 14.73 | 74.59 |
| | 1st Zn cl tail | 12.07 | 1.05 | 0.13 | 3.84 | 4.74 | 15.42 | 6.92 |
| | 2nd Zn cl tail | 2.38 | 1.77 | 0.17 | 5.95 | 1.57 | 3.93 | 2.11 |
| | Pyrite conc | 14.41 | 0.53 | 0.09 | 2.77 | 2.86 | 12.77 | 5.96 |
| | Tail | 50.23 | 0.04 | 0.02 | 0.09 | 0.75 | 9.82 | 0.67 |
| | Feed | 100.00 | 2.67 | 0.01 | 6.70 | 100.00 | 100.00 | 100.00 |
| | Py. conc & tail | 64.64 | 0.15 | 0.04 | 0.69 | 3.61 | 22.59 | 6.63 |

copper assays. It is likely that some of the free chalcopyrite grains were lost as slimes during copper cleaner operations due to overgrinding, but were later recovered during zinc flotation stages where conditions could be more favorable for the flotation of chalcopyrite slimes.

It was surprising to see that chalcopyrite remained readily floatable in the cleaners after the 30 minutes of regrind without adding $Na_2S$ (Test TA-4). Although $Na_2S$ was added in Test TA-5 during the 50 minute regrind, it was found in another test that the 50 minute grind without $Na_2S$ gave a good grade (24.39% Cu) concentrate with a respectable recovery (78.4%). This finding appears to be in conflict with the Heyes and Trahar's report (1977) that clean chalcopyrite ground in an iron mill does not float unless the oxidation potential is raised either by aeration or by addition of oxidants.

*c. Use of Kerosene*

Test TA-5 was repeated in Test TA-6 using kerosene. The hydrocarbon oil was added at the following points of the flowsheet (see Fig. 4); copper rougher (0.08 lb/ton), copper scavenger (0.04 lb/ton), first copper cleaner (0.04 lb/ton), and zinc rougher (0.16 lb/ton). The reagent balance and the flowsheet remained essentially the same with a few minor modifications: First, the amount of frother (DF 1200) added was cut down by one half of that used in Test TA-5. Second, the zinc rougher concentrate was cleaned three times, the first and second cleaners by using 1000 g cells because of the thick froth produced by the hydrocarbon oil. Finally, 0.10 lb/ton

of KAX was used for the pyrite flotation. Table VII shows that the copper recovery (86.41%) of Test TA-6 was an improvement over that of Test TA-5 (82.73%), but the copper concentrate assayed only 17.47% Cu, which was considerably lower than that of Test TA-5 (23.57%). Apparently kerosene was used in excessive amount during the chalcopyrite flotation, which resulted in a decrease of selectivity; both pyrite and sphalerite (13.9% of the total Zn) floated with the chalcopyrite. The use of kerosene showed its benefit, however, during sphalerite flotation: The zinc recoveries of Test TA-5 and TA-6 are almost identical (74.6% v.s. 74.3%), but a higher grade zinc concentrate (47.34% Zn) was obtained in Test TA-6. This was a rather significant improvement considering that Test TA-6 had in effect a lower zinc feed (86.6% of the total zinc) than test TA-5 (90.3% of the total zinc) by taking the zinc loss in the final copper concentrate into account. The effective zinc recovery of Test TA-6 was, therefore, 85.8% with a grade of 47.34% Zn, while in Test TA-5 it was 82.6% with a lower grade (43.4% Zn).

The use of kerosene adds another significant benefit to the collectorless flotation. The flotation time of the rougher flotation was substantially shortened particularly in the zinc flotation. It was observed that the zinc rougher flotation tended to be sluggish as compared to the copper rougher flotation, which is most likely due to the fact that finer grinding was necessary for the improved flotation recovery of

TABLE VII: Results of Test TA-6

| Test No. and Remarks | Product | Weight (%) | Assay's (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TA-6<br><br>Test conditions are similar to these of Test TA-5, except that kerosene is used and zinc rghr. conc. was cleaned three times. | Cu conc | 12.76 | 17.47 | 0.33 | 7.02 | 86.41 | 37.46 | 13.38 |
| | Zn conc | 10.50 | 1.27 | 0.39 | 47.34 | 5.17 | 36.48 | 74.29 |
| | 3rd Zn cl tl | 1.27 | 1.34 | 0.16 | 4.88 | 0.66 | 1.78 | 0.92 |
| | 2nd Zn cl tl | 8.84 | 0.81 | 0.11 | 4.10 | 2.78 | 8.63 | 5.42 |
| | 1st Zn cl tl | 3.06 | 0.90 | 0.13 | 3.15 | 1.07 | 3.56 | 1.44 |
| | Pyrite conc | 8.99 | 0.76 | 0.09 | 2.35 | 2.65 | 7.21 | 3.16 |
| | Tail | 54.57 | 0.06 | 0.01 | 0.17 | 1.27 | 4.89 | 1.39 |
| | Feed | 100.00 | 2.58 | 0.11 | 6.69 | 100.00 | 100.00 | 100.00 |

sphalerite. When the copper rougher tail was not reground prior to the zinc rougher flotation as in Test TA-3, sphalerite floated as fast as chalcopyrite.

*d. Effect of Aerative Conditioning with $SO_2$.*

At the Texasgulf concentrator, the copper-zinc separation is effected by aeration with lime and conditioning with $SO_2$ (Amsden 1974). This same technique may be adopted in the collectorless flotation. Tests TA-7 and TA-8, respectively, were made with and without the aerative conditioning by keeping other experimental conditions identical. In Test TA-7, the feed ore (-20 mesh) was ground for 70 minutes with no reagents (Fig. 5). The ground ore (78% passing 500 mesh as determined by the screen analysis of the final tailing) was aerated for 15 minutes at a 20% pulp density after the addition of $SO_2$, and diluted to the volume of a 1000g flotation cell, which gave a pH of 7.0. The remainder of the test procedures is shown in the Flowsheet (Fig. 5), which is self-explanatory. The potassium permanganate added during the first zinc cleaner was to help suppress pyrite.

Table VIII represents the results of the Test TA-7 and TA-8. A significant improvement made by the aerative conditioning with $SO_2$ was that the zinc loss in the final copper concentrate was reduced from 8.9% of the total zinc content to 4.1%. Perhaps more sig ificant was that the grade of the final zinc concentrate was improved from 37.33% Zn to 52.50% Zn. The zinc recovery in the final concentrate was reduced slightly, but the recovery of the zinc rougher flotation was improved by

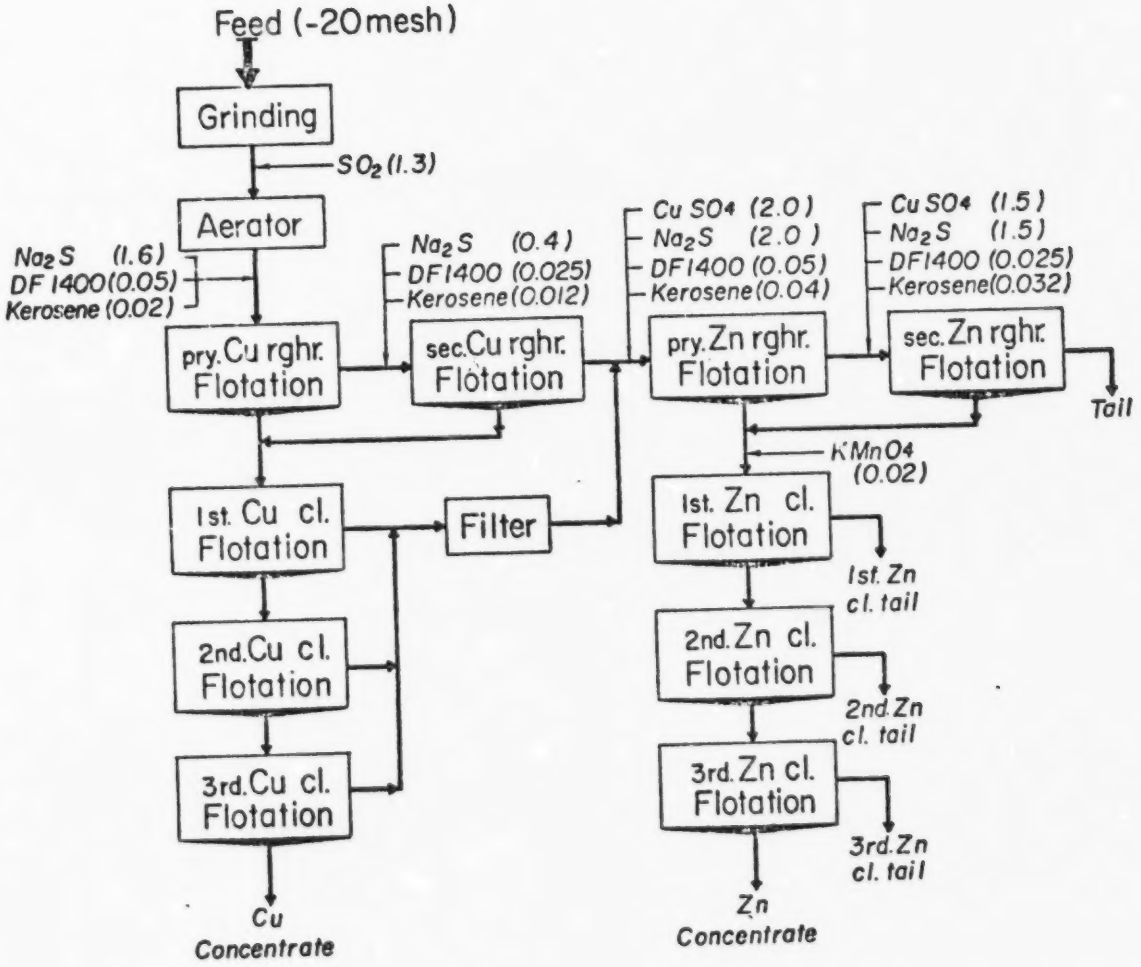


Fig. 5. Laboratory flowsheet and reagent balance (lb/ton) of test TA-7.

TABLE VIII: Results of Test TA-7 and TA-8

| Test No. and Remarks | Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TA-7<br>Collectorless flotation after aerative conditioning with $SO_2$. | Cu conc | 8.84 | 23.71 | 0.35 | 3.54 | 78.45 | 29.15 | 4.09 |
| | Zn conc | 9.38 | 1.94 | 0.25 | 52.50 | 6.81 | 22.17 | 77.66 |
| | 3rd Zn cl tail | 1.06 | 3.52 | 0.53 | 14.72 | 1.40 | 5.28 | 2.46 |
| | 2nd Zn cl tail | 4.21 | 2.03 | 0.21 | 7.82 | 3.20 | 8.30 | 5.19 |
| | 1st Zn cl tail | 13.26 | 1.28 | 0.09 | 2.71 | 6.35 | 11.23 | 5.67 |
| | Tail | 63.25 | 0.16 | 0.04 | 0.41 | 3.79 | 23.87 | 4.93 |
| | Feed | 100.00 | 2.67 | 0.11 | 6.34 | 100.00 | 100.00 | 100.00 |
| Test TA-8<br>Collectorless flotation without aerative conditioning with $SO_2$. | Cu conc | 8.91 | 23.24 | 0.38 | 6.53 | 81.80 | 4.97 | 8.91 |
| | Zn conc | 13.78 | 1.34 | 0.19 | 37.33 | 7.29 | 3.84 | 78.77 |
| | 3rd Zn cl tail | 1.59 | 3.13 | 0.27 | 12.31 | 1.97 | 63.07 | 3.02 |
| | 2nd Zn cl tail | 1.02 | 1.64 | 0.16 | 5.49. | 0.66 | 23.83 | 0.85 |
| | 1st Zn cl tail | 9.83 | 1.01 | 0.10 | 2.97 | 3.92 | 1.44 | 4.47 |
| | Tail | 64.86 | 0.17 | 0.03 | 0.40 | 4.36 | 2.86 | 3.97 |
| | Feed | 100.00 | 2.53 | 0.10 | 6.53 | 100.00 | 100.00 | 100.00 |

almost 4%. The beneficial effect of the aerative conditioning with $SO_2$ on the collectorless flotation of sphalerite is demonstrated by the recovery vs grade curves of tests TA-7 and TA-8 in Fig. 6 (curves B and C, respectively).

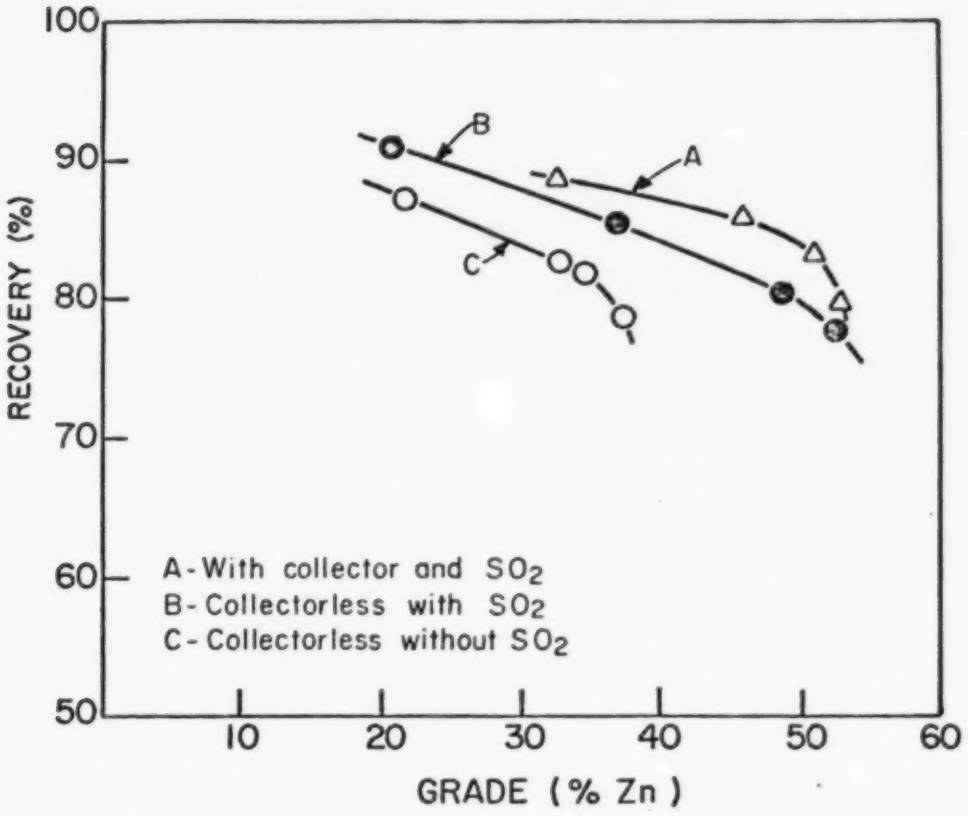


Fig. 6. Recovery v.s. grade curves for Tests TA-7, -8, and -9.

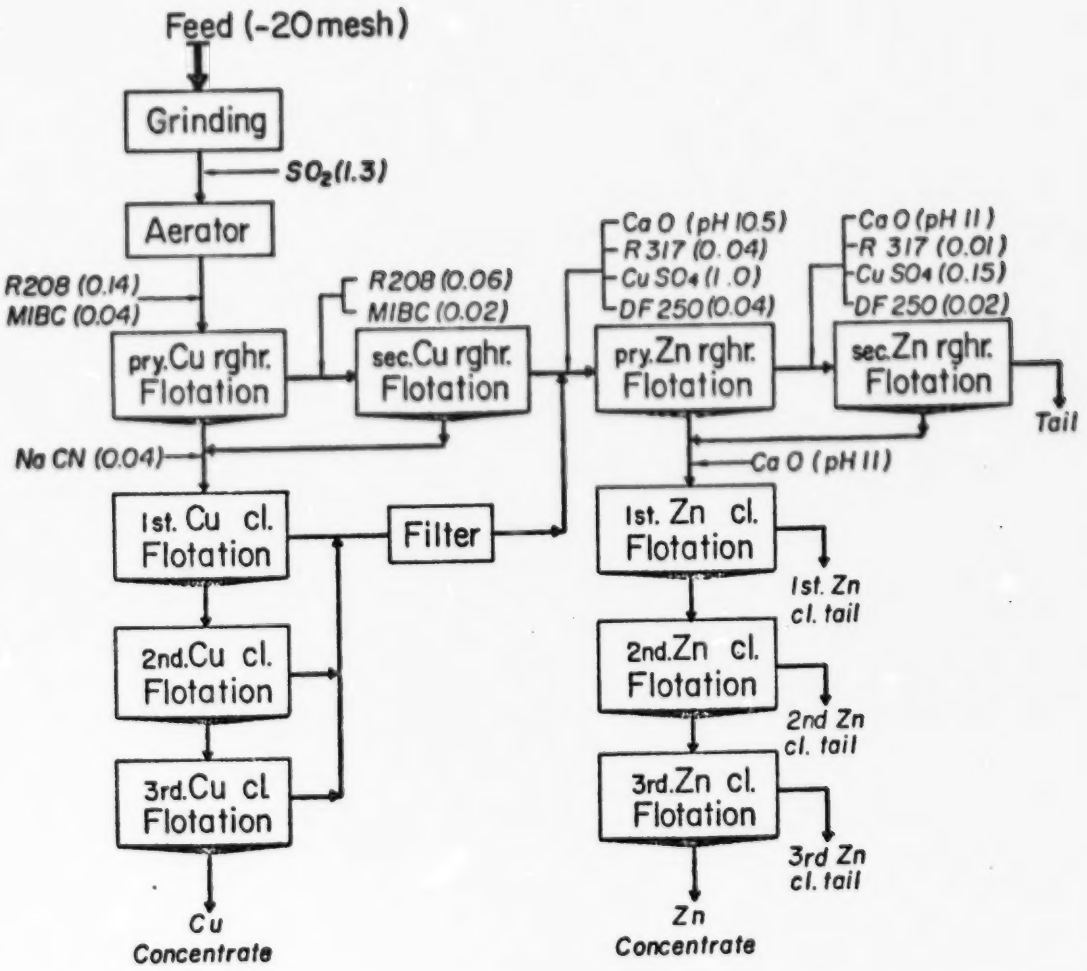


Fig. 7. Laboratory flowsheet and reagent balance (lb/ton) of test TA-9.

*e. Comparison between Collectorless and Conventional Flotation*

Fig. 7 represents the flowsheet of Test TA-9, which was conducted by using conventional thiol-type collectors. Attempts were made during the test to follow the reagent balances used at the Texasgulf concentrator as closely as possible. The conditions for grinding and aeration were identical to those of Test TA-7. Reagent 208 (sodium dithiophosphate) and reagent 317 (sodium isobuthyl xanthate) were used as collectors. A 10 minute conditioning period was allowed after each addition of collectors. The flotation at each stage was conducted until exhaustion, as in Test TA-7, in order to obtain the maximum recovery.

The results of Test TA-9 are given in Table IX, which may be compared with the results of test TA-7 (Table VIII). The copper recovery of the conventional flotation was better than that of the collectorless flotation, but it has been shown already that, after coarser grinding, the collectorless flotation technique can produce a commercial grade concentrate with acceptable recovery (e.g. Test TA-3, Table V).

The zinc flotation in Tests TA-9 and TA-7 may be best compared by the recovery v.s. grade curves (curves A and B, respectively) given in Fig. 6. The final zinc concentrates of the two tests are practically of the same grade, but the recovery obtained by the convential technique was higher by about 2%. Note, however, that the zinc rougher recovery of the collectorless flotation was considerably higher (by 3.9%) than that of the

TABLE IX: Results of Test TA-9

| Test No. and Remarks | Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TA-9<br>Flotation using R 308 and R 317 after aerative conditioning with $SO_2$. | Cu conc | 8.54 | 25.48 | 0.47 | 4.68 | 83.70 | 39.88 | 6.19 |
| | Zn conc | 9.73 | 2.82 | 0.09 | 52.96 | 10.55 | 8.73 | 79.78 |
| | 3rd Zn cl tail | 0.79 | 0.08 | 0.05 | 0.46 | 1.10 | 3.07 | 3.43 |
| | 2nd Zn cl tail | 1.39 | 3.62 | 0.39 | 28.05 | 1.01 | 3.87 | 2.54 |
| | 1st Zn cl tail | 5.56 | 0.64 | 0.14 | 3.24 | 1.37 | 7.74 | 2.79 |
| | Tail | 73.99 | 0.08 | 0.05 | 0.46 | 2.27 | 36.71 | 5.27 |
| | Feed | 100.00 | 2.60 | 0.10 | 6.46 | 100.00 | 100.00 | 100.00 |

conventional flotation. This may be an encouraging aspect of the collectorless flotation in that by recirculating the middlings in a continuous operation the final zinc recovery can be improved considerably. Furthermore, if one can find a proper pyrite depressant, which can be used for the cleaning operation, such as lime in conventional flotation (see Fig. 7), the collectorless flotation could potentially produce much improved results even in a batch flotation test. The use of $KMnO_4$ during the first cleaner of Test TA-7 (see Fig. 5) seemed to help suppress pyrite, but it was not optimized.

C. Texasgulf Type 'C' Ore

a) Effect of $KMnO_4$ on the Collectorless Flotation of Sphalerite.

Fig. 8 represents the flowsheet of Test TC-1. When the ore (-20 mesh) was ground for 25 minutes without any reagents and transferred to a flotation cell, a considerable portion of galena was found to 'skin-float'. An attempt was, therefore, made to recover galena by adding frother alone. Chalcopyrite was then floated in two stages by adding $Na_2S$ and DF 1400. The copper/lead concentrates were combined and cleaned once. Results of the copper/lead flotation were poor as shown in Table X, which may be largely due to the coarse ginding.

Zinc rougher flotation was done on the copper scavenger tail by adding $Na_2S$, $CuSO_4$ and DF 1400. The zinc rougher tail was filtered and reground for one half hour prior to the first and second zinc regrind flotation. The three zinc concentrates were combined, as shown in Fig. 8, and

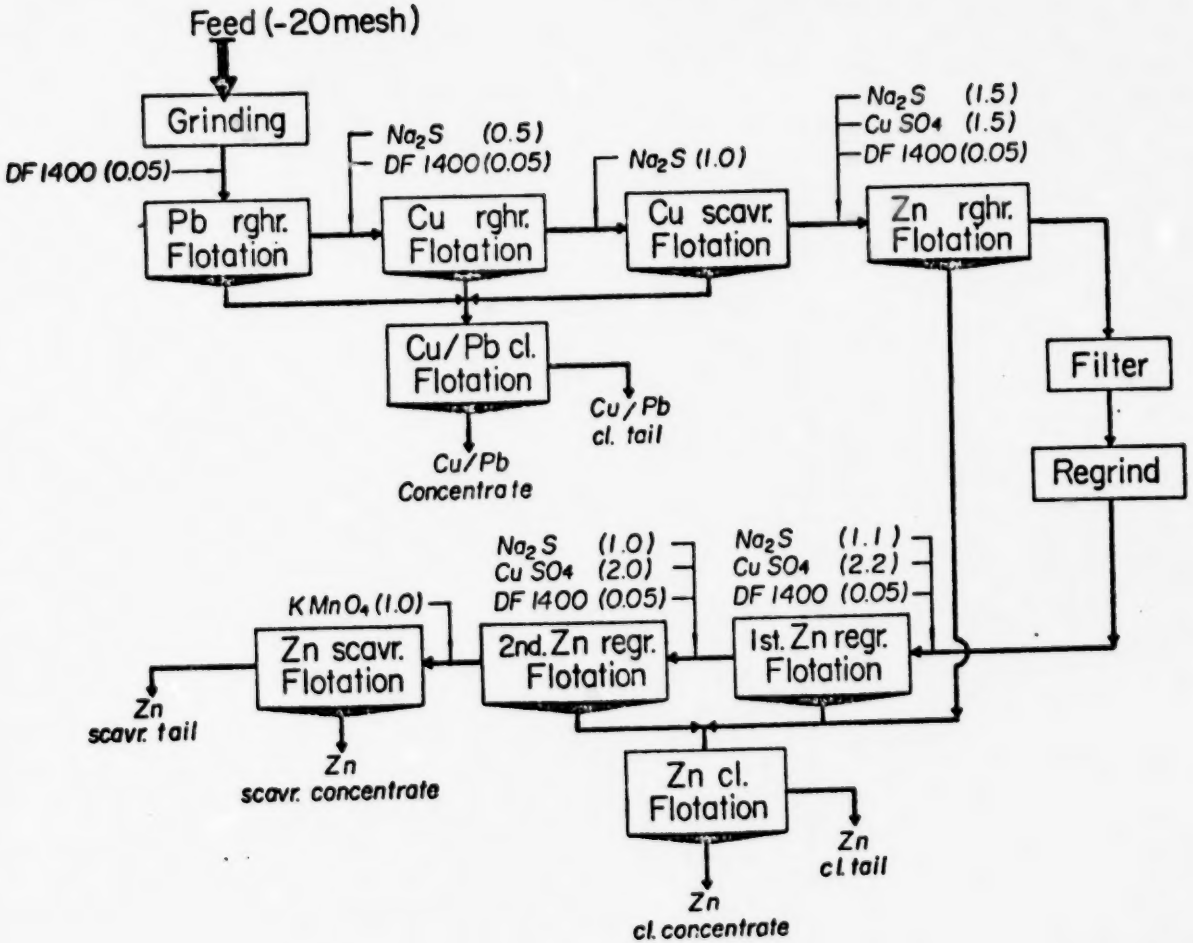


Fig. 3. Laboratory flowsheet and reagent balance (lb/ton) of test TC-1.

TABLE X: Results of Test TC-1

| Test No. and Remarks | Products | Weight (%) | Assays | | | Distribution | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TC-1<br>Feed (-20 mesh) ground for 25 min. Zn rghr. tail reground for 30 min., $KMnO_4$ was used for Zn scavr. Collectorless flotation. | Cu/Pb conc | 8.43 | 1.88 | 1.82 | 8.44 | 37.37 | 15.34 | 71.15 |
| | Cu/Pb tail | 5.39 | 0.33 | 0.98 | 10.52 | 4.20 | 7.28 | 6.04 |
| | Zn cl conc | 9.01 | 0.66 | 1.66 | 41.07 | 14.03 | 20.64 | 39.98 |
| | Zn cl tail | 8.73 | 0.28 | 1.07 | 6.77 | 5.75 | 12.88 | 6.29 |
| | Zn scavr conc | 6.71 | 0.97 | 0.98 | 40.76 | 15.35 | 9.08 | 29.13 |
| | Zn scavr tail | 61.73 | 0.16 | 0.34 | 1.67 | 23.30 | 28.96 | 10.98 |
| | Feed | 100.00 | 0.42 | 0.72 | 9.34 | 100.00 | 100.00 | 100.00 |

cleaned once to produce a zinc concentrate assaying 41.67% Zn with the recovery of 39.98% (Table X). An interesting observation was made, in this case, when 1.0 lb/ton of $KMnO_4$ was added to the cell after the second zinc regrind flotation: After 10 minutes conditioning of clean zinc scavenger concentrate was obtained which assayed 40.76% Zn with a recovery of 29.13%. This was a puzzling observation, considering that sphalerite could be oxidized by $KMnO_4$ and loose its natural floatability. Nevertheless, the beneficial effect of $KMnO_4$ on sphalerite flotation was observed repeatedly in the ensuing tests particularly when excess $CuSO_4$ was used. It is noted, however, that when $KMnO_4$ was added in excessive amount the flotation was completely suppressed.

b. Comparison between Collectorless Flotation and Conventional Flotation

Fig. 9 shows the results of two sphalerite flotation tests conducted with Texasgulf type 'C' ore. Curve A represents the result of a conventional flotation test conducted by using R208, R317, $CuSO_4$, lime soda ash, DF250 and $SO_2$/aeration. Curve B represents the results of collectorless flotation test conducted by using $Na_2S$, $CuSO_4$, DF 1400, diesel oil and $KMnO_4$. The collectorless flotation test did not employ the $SO_2$/aeration technique, which was found in test TA-7 to significantly improve the sphalerite flotation. In both tests the feed ore (-20 mesh) was ground for 70 minutes (77% passing 500 mesh), and the copper/lead concentrate was produced prior to the zinc rougher flotation.

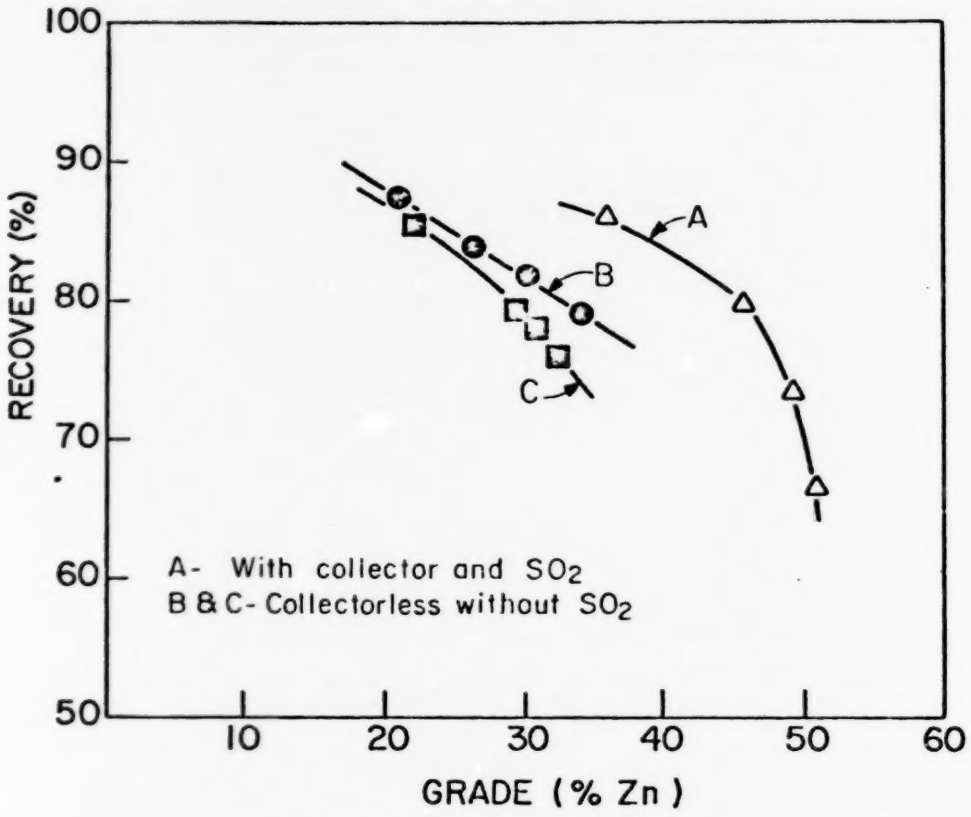


Fig. 9. Recovery v.s. grade curves for the flotation of sphalerite from Texasgulf type 'C' ore with and without using collectors.

With the type 'C' ore the conventional flotation appears to be superior to the collectorless flotation, although the zinc recovery in the final concentrate, assaying 50.94% Zn, was only 66.5% (Fig. 9). It is possible, however, that the collectorless flotation could have produced a comparable final zinc concentrate if a few more cleaning operations had been

made. Also, it is rather unfortunate to note here that due to a shortage of test samples no collectorless flotation test was made with the Texasgulf type 'C' ore by employing the aerative conditioning with $SO_2$, which in view of Test TA-7 could have produced a better result than the one shown in Fig. 9.

D. Collectorless Flotation without using $Na_2S$.

A collectorless flotation test was made without using $Na_2S$ in order to demonstrate that the use of such a cleaning agent was essential (Test TA-10). Texasgulf type 'A' ore was ground for 70 minutes and floated as shown in Fig. 10. After one cleaning operation a copper concentrate assaying 16.68% Cu was obtained with a recovery of 71.76% (Table XI). It should also be pointed out that the chalcopyrite was extremely slow-floating, so that the copper rougher flotation took a total of 45 minutes in five stages. Also, the amount of frother needed was five times as much as when $Na_2S$ was used. Moreover, a large amount of pyrite floated with chalcopyrite during the rougher flotation stage due to the lack of selectivity.

When 2.0 lb/ton of $CuSO_4$ was added to the copper rougher tail, a considerable amount of sphalerite was found to float readily, but a large portion of sphalerite was retained in the tailing. After one cleaning, a zinc concentrate assaying 36.35% Zn was obtained with a mere recovery of 28.46%. In the zinc scavenger flotation, another 2.0 lb/ton of copper sulphate was first added together with DF 1400 in an attempt to float

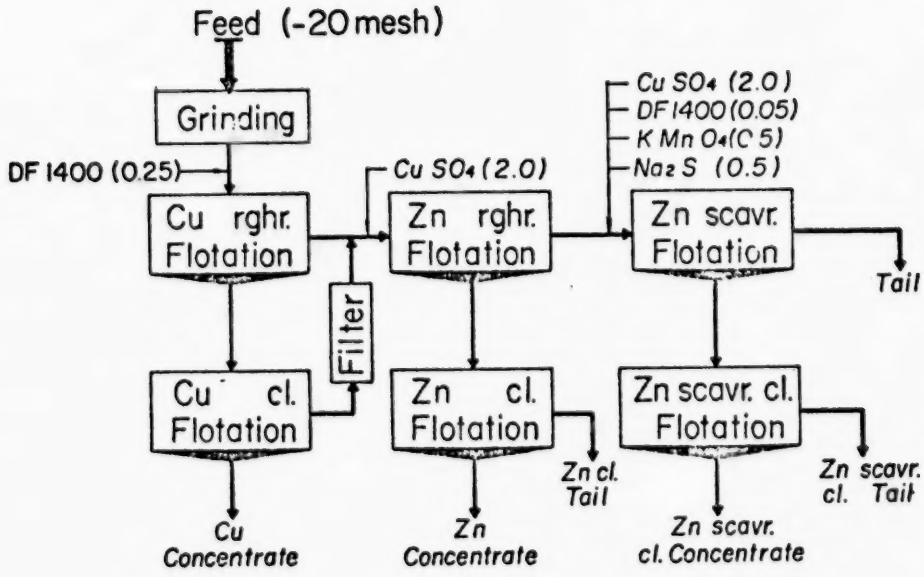


Fig. 10. Flowsheet and reagent balance (lb/ton) of test TA-10.

TABLE XI: Results of Test TA-10

| Test No. and Remarks | Products | Weight (%) | Assays (%) | | | Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | Cu | Pb | Zn | Cu | Pb | Zn |
| Test TA-10<br>$Na_2S$ was used only for Zn scavr. flotation. | Cn conc | 11.04 | 16.68 | 0.35 | 7.16 | 71.76 | 37.59 | 12.35 |
| | Zn conc | 5.01 | 5.26 | 0.37 | 36.35 | 10.27 | 18.01 | 28.46 |
| | Zn cl tail | 5.76 | 1.55 | 0.12 | 6.39 | 3.48 | 6.27 | 5.75 |
| | Zn sc cl conc | 6.22 | 1.05 | 0.12 | 39.87 | 2.54 | 7.30 | 38.75 |
| | Zn sc cl tail | 4.91 | 1.19 | 0.09 | 5.49 | 2.28 | 4.28 | 4.21 |
| | Tail | 67.06 | 0.37 | 0.04 | 1.00 | 9.67 | 26.10 | 10.48 |
| | Feed | 100.00 | 2.57 | 0.10 | 6.40 | 100.00 | 100.00 | 100.00 |

more sphalerite from the zinc rougher tailing, but to no avail. Considering the possibility that the second dosage of copper sulphate might have caused the suppresion of sphalerite, $KMnO_4$ was then added, since it was found in Test TC-1 that the oxidant reactivated the sphalerite suppressed by the excessive use of copper sulphate, but without success. However, when $Na_2S$ was finally added to the tailing, good flotation of sphalerite occurred. After one cleaning, a zinc scavenge cleaner concentrate assaying 39.87% Zn was obtained with a recovery of 38.8% (Table XI).

## DISCUSSION

It has been established in the present work that both chalcopyrite and sphalerite can be floated successfully without using a collector if the ore is treated with a cleaning agent such as $Na_2S$ to remove the surface oxidation products. This is similar to the finding by Ravitz and Porter (1943) that galena floats well without collector in a microflotation cell once the surface is cleaned by using ammonium acetate. Thus, the results of the present investigation appear to support the old concept that sulphide minerals are intrinsically hydrophobic. Although it is not the purpose of this investigation to prove this assumption, it may be fruitful to disucss the possible causes for the apparent hydrophobicity of sulphide minerals.

A. Possible Causes for Collectorless Flotation

First, one must consider the possible contamination of ore samples during grinding, flotation or by the impurities of the reagents used. It is difficult, however, to conceive that contamination of such origins can account for the reproducible results of the flotation tests handling large quantities of ore samples.

Second, elemental sulphur, a well recognized hydrophobic entity (Finkelstein, et al, 1975), may be deposited on the surface by the oxidation of sulphide minerals themselves or by the oxidation of sulphide ions introduced as $Na_2S$. This possibility is not favored, however, since both chalcopyrite and sphalerite float well at an alkaline pH, at which elemental sulphur is thermodynamically unstable (Garrels and Christ, 1965).

Third, the frothers used in the present work might have a collecting power. Heyes and Trahar (1977), who used PPG400* in their collectorless flotation tests with chalcopyrite, were skeptical, however, of its collecting power on the ground that it has no active functional groups. Whilst a frother is not likely to induce hydrophobicity, it could absorb through van der Waals forces on a surface, which already has become hydrophobic as a result of treating the surface of the sulphide mineral with $Na_2S$. Since adsorption of this type is generally an entropic process (Yoon 1977), the adsorption of a frother would become more favorable with increasing molecular weight. This could account for the experimental observation that collector-

* Polypropylene glycol, which is same as the DF series used in in the present work.

less flotation was improved by switching from DF 250 to DF 1400 and by using hydrocarbon emulsions. It could also offer an explanation for the Heyes and Trahar's finding (1977) that the floatability of clean chalcopyrite was 35% with no frother, 60% with amyl alcohol and nearly 100% with PPG 400 in a Hallimond Tube. In this limited sense, the frothers used in a collectorless flotation could be regarded as having a collecting power.

A fourth possibility may be that the apparent hydrophobicity of sulphide minerals is due to oxygen adsorption which promotes the dehydration of the surface (Plaksin 1949, Plakin and Shafeev 1960). Further action of oxygen could then lead to the oxidation of the sulphide mineral accompanied by the development of water repellent properties (Glembotskii et al 1963). Supportive evidence are the observations that dry-ground chalcopyrite can be floated without collector (Lepetic 1974), and that chalcopyrite ground in an iron mill does not float without collector unless an oxidizing environment is created (Heyes and Trahar 1977). Note, however, that $Na_2S$ which is a reducing agent has been found to promote the collectorless flotation of chalcopyrite, although the oxidation potential of the present system has not been measured.

Plaksin's theory may be further elaborated by using the oxidation mechanism for galena proposed by Eadington and Prosser (1969). At the initial stage of oxidation (induction period) it is assumed that oxygen is rapidly chemisorbed from solution with a partial transfer of electrons from the solid

to oxygen molecules or atoms. There follows a slow process in which further electron transfer occurs to form $O^{2-}$ or, perhaps $O_2^{2-}$ initially, which reacts with water and desorbs as $OH^-$, or $H_2O_2$ and $OH^-$. The positive holes left in the lead sulphide associate with sulphide ions to form neutral sulphur atoms which remain in the lead sulphide lattice. Simultaneously, the lead sulphide surface loses a lead ion to the solution. The overall reaction is represented by the following equation,

$$PbS + O_{(surface)} + H_2O \longrightarrow Pb^{2+}_{(aq)} + S_{(PbS)} + 2OH^-_{(aq)} \quad \ldots[1]$$

which will proceed until the outer layers of the lead sulphide crystal become supersaturated with sulphur (or excess sulphide ions). It is perhaps the sulphur-rich surface that is responsible for the apparent hydrophobicity of a sulphide mineral. In the later stage of oxidation the elemental sulphur, nucleated on the supersaturated surface in pockets, may be oxidized into thiosulphate and sulphate, which are hydrophilic. The sulphide mineral would then lose its apparent hydrophobicity.

Finally, one may consider the old concept that sulphide minerals are intrinsically hydrophobic. The strongest evidences were presented by Ravitz and Porter (1933), Ravitz (1940) and Fuerstenau (1975), who showed that clean sulphide minerals were floatable in the absence of oxygen. Leja (1977) has pointed out, however, that it is a difficult task to create an absolutely oxygen-free atmosphere and that a minute amount of oxygen is probably sufficient to alter the floatability of sulphide

minerals. The latter view is supported by the work of Hillenbrand (1969).

Obviously the last two mechanisms above are mutually exclusive, but both are more likely ones than the others discussed. It is difficult to resolve which of the two mechanisms is indeed operative in a collectorless flotation on the basis of the present investigation, since the experimental parameters affecting the flotation have not been sufficiently isolated from one another. The essential feature that is common in both mechanisms is, however, that collectorless flotation is obtainable only if the surface is relatively free of oxidation products, which justifies the use of cleaning agents such as $Na_2S$. Test TA-10 has proven that both chalcopyrite and sphalerite are difficult to float without using a cleaning agent.

B. Cleaning Action of Sodium Sulphide

Ravitz and Porter (1933) cautiously offered an interesting conjecture: "May not the function of xanthate be, in part, that of a cleaning agent; i.e., to remove oxidation products from the surface of the mineral, leaving the nonpolar sulphide free for the displacement of water by gas?" This theory received criticisms by Sutherland and Wark (1955b), which is understandable in view of the modern theories of oriented collector adsorption. It should be pointed out, however, that the cleaning action of xanthate has been proven already by Taggart,et al (1930) and Taylor and Knoll (1935). They showed that oxidation products are stoichiometrically displaced by

xanthate ions from galena surface by a well defined ion-exchange mechanism. Also, the quantity of oxidation products removed, or the quantity of xanthate ions taken up, increases with the extent to which the galena sample has been given an opportunity to oxidize (Gaudin 1957). Yoon (1977) measured up to eleven monolayer equivalent, of xanthate adsorption on a heavily oxidized galena sample, while Herd and Ure (1941) and Knoll and Baker (1941) showed that unoxidized galena had no ion exchange capacity and is not floated by alkali xanthates. What is likely wrong with the Ravitz and Porter's suggestion above is, however, that water was considered to be displaced by gas at the clean sulphide surface, while modern theories suppose that the displacement occurs at the hydrocarbon ends of the adsorbed collector species.

In view of the cleaning actions of both xanthate and sulphide ions, it is tempting to adopt the ion-exchange mechanism for xanthate adsorption in explaining some of the collectorless flotation results obtained in the present work. The following equation may represent the sulphidization of oxidized sulphide minerals,

$$\boxed{\begin{matrix}M^{2+} & A^{2-} \\ \text{Sulphide Mineral}\end{matrix}} + 2Na^{+} + S^{2-} \longrightarrow \boxed{\begin{matrix}M^{2+} & S^{2-} \\ \text{Sulphide Mineral}\end{matrix}} + 2Na^{+} + A^{2-} \quad \ldots[2]$$

in which $M^{2+}$ represents the metal ion of the sulphide mineral and $A^{2-}$ the oxidation products such as $SO_4^{2-}$, $S_mO_n^{2-}$, $O^{2-}$ and

$2OH^-$. Eq. [2] will proceed from left to right, because most oxidation products (MA) are much more soluble than the substrate (MS). The sulphide mineral cleaned of its oxidation products may have its natural floatability, which had been hampered by the hydrophilic oxidation products, restored (Ravitz and Porter, 1933).

TABLE XII: Solubility Equilibria for Common Sulphide Minerals at 25°C

| Minerals | $\Delta G°_f$ (Kcal/ Mole) | Equilibria | No. | $pK_{so}$ |
|---|---|---|---|---|
| Chalcopyrite | -45.55* | $CuFeS_2 = Cu^{2+} + Fe^{2+} + 2S^{2-}$ | 1 | 62.10 |
| Covellite | -12.73* | $CuS = Cu^{2+} + S^{2-}$ | 2 | 36.82 |
| Galena | -22.15† | $PbS = Pb^{2+} + S^{2-}$ | 3 | 28.08 |
| Sphalerite | -47.4† | $ZnS = Zn^{2+} + S^{2-}$ | 4 | 25.06 |
| Pyrite | -39.84† | $FeS_2 = Fe^{2+} + S_2^{2-}$ | 5 | 28.80 |
| | | $= Fe^{2+} + S^{o} + S^{2-}$ | 6 | 30.43 |
| Pyrrhotite | -23.32† | $FeS = Fe^{2+} + S^{2-}$ | 7 | 18.31 |

$\Delta G°_f$; Standard free energy of formation. $pK_{so}$; solubity product. * King, Mah and Pankratz (1973). † Latimer (1961). $\Delta G°_f$'s for ions in Kcal/mole; $Cu^{2+}$ (15.53), $Fe^{2+}$ (-20.3), $Pb^{2+}$ (-5.81), Zn (-35.184), $S^{2-}$ (21.96), $S_2^{2-}$ (19.75), $S^{o}$ (0) (Garrels and Christ, 1965).

C. Selective Flotation of Chalcopyrite from pyrite and Pyrrhotite

Both chalcopyrite and pyrite, cleaned by freshly prepared ammonium sulphide solution, showed 100% floatability

in a microflotation cell even in the absence of a frother. An interesting question arises, then, as to how the selective flotation of chalcopyrite has been made possible in the present work from ore samples which contain 20 to 35% pyrite. In an attempt to answer this question, the solubility products of common sulphide minerals are listed in Table XII. It shows that the two copper minerals are least soluble of all the sulphides listed. The solubility of chalcopyrite is difficult to compare with the others by $pK_{so}$ values alone, but it has been shown that the minimum solubility of chalcopyrite is about $5.0 \times 10^{-14}$ moles/l at pH 8.0 in a closed, oxygen free system while that of sphalerite is about $10^{-10}$ moles/l at pH 7.5 (Yoon 1978a). Therefore, if a mixture of common sulphide minerals is treated by a $Na_2S$ solution of relatively low concentration, the copper minerals will be sulphidized in preference to the others, assuming that all the minerals in the mixture are oxidized to the same extent. It appears, then, that collectorless flotation of the copper minerals is most favoured, particularly with respect to pyrrhotite which is the most soluble (Eg. 7, Table XII). The sulphidization of pyrite is thermodynamically favorable in view of its relatively low solubility, but it appears to be a kinetically slow process: it may have to go through the following step,

$$S^{2-} + S^{\circ} \xrightarrow{K} S_2^{2-}, \quad K = 10^{1.62}, \qquad \ldots [3]$$

which involves elemental sulphur. It is well recognized

that most low temperature reactions involving elemental sulphur as a intermediary product, such as the oxidation of sulphide minerals, are slow processes (Eadington and Prosser 1969).

Another possible explanation for the selective flotation of chalcopyrite is that perhaps it has a lower degree of oxidation than other sulphides in an ore. If this is the case, its sulphidization would be completed well ahead of the other sulphide minerals and it would float first. It has been shown in our laboratory that once chalcopyrite is cleaned of its oxidation products, it is difficult to reoxidize it to the extent that its natural floatability disappears: After 1½ hours of aqueous oxidation at pH 10 by blowing a stream of air through the suspension, the floatability of chalcopyrite was 76.3%, while the floatability of pyrite was reduced from 100% to 8.3% after oxidation under identical conditions (Yoon 1978b). The strong resistance of chalcopyrite to oxidation has manifested itself also in the present work: good copper recoveries have been achieved in the cleaners after 30 to 50 minutes of regrinding the rougher concentrates.

By lowering the pH to about 6 during or after sulphidization, higher grade copper concentrates have been obtained. A possible explanation might be that the amount of excess $S^{2-}$ and/or $HS^{-}$ ions available for the sulphidization of pyrite are reduced significantly as the pH becomes lower than the system point (pH = $pK_a$ = 7.1) below which $H_2S$ is a more stable form of sulphur (Barnes et al 1967). The sulphidization of chalcopyrite may also be adversely affected by lowering the pH below

the system point, but likely to a lesser extent than that of pyrite due to the lower $pK_{so}$ of chalcopyrite.

D. Activation of Sphalerite and the Effect of Aerative Conditioning

Results of the present work have shown that the collectorless flotation of sphalerite does not occur unless it is activated by cupric ions. Apparently, clean sphalerite has substantially less natural floatability than other common sulphide minerals: it has been shown in our laboratory that a sphalerite sample cleaned by $(NH_4)_2S$ solution floats only 38.7%, while Finkelstein et al (1975) have shown that freshly crushed sphalerite floats less than 5% without collector. Sutherland and Wark (1955c) explained the activation mechanism by the following reaction,

$$ZnS + Cu^{2+} \longrightarrow CuS + Zn^{2+}, \qquad K = 10^{11.76} \qquad ...[4]$$

in which K has been determined from the thermodynamic data given in Table XII. In view of Eq. [4], the collectorless flotation of activated sphalerite should be attributed to the CuS coating, which may be naturally hydrophobic when it is freshly deposited.

Sutherland and Wark (1955d) have noted that unoxidized pyrite abstracts cupric ions as much as sphalerite does. Also, Chang et al (1954) have shown that pyrrhotite, which is not readily floated at alkaline pH by potassium amyl xanthate (Rojo, 1978), can be activated by cupric ions. The abstraction of copper by these iron minerals may be represented by the following reactions in view of Eq [4],

$$FeS + Cu^{2+} \longrightarrow CuS + Fe^{2+}, \qquad K = 10^{18.51}, \qquad \ldots [5]$$

and

$$FeS_2 + Cu^{2+} \longrightarrow CuS + S^{\circ} + Fe^{2+}, \qquad K = 10^{6.39} \qquad \ldots [6]$$

which show that the CuS coatings on pyrite and particularly on pyrrhotite are thermodynamically possible. Assuming the fresh CuS coatings on pyrrhotite and pyrite are as hydrophobic as that formed on a sphalerite surface, one should not expect a good separation between sphalerite and the two iron minerals in a collectorless flotation. In fact, the same problem should be encountered in a conventional flotation using thiol-type collectors. However, if pyrite is oxidized, the copper abstraction and, hence, the CuS coating may be prevented, which is probably why aerative conditioning precedes zinc flotation in most mills. The fact that the collectorless flotation of sphalerite has been improved significantly in Test TA-7, can be explained in a similar fashion. It is unfortunate that due to the shortage of test samples only one test was made with aerative conditioning.

E. Considerations on Reagent Consumption

During the collectorless flotation of sphalerite, it was found that a proper balance of reagents between copper sulphate and sodium sulphide was critical to the success of a test. If one was added in too great excess, the flotation was often completely suppressed. However, it did not seem to matter which one was added first. Hence, if the flotation appeared to be suppressed by the excessive addition of copper

sulphate, more sodium sulphide was added to balance it, which normally restored the flotation. The optimum copper sulphate to sodium sulphide ratio has yet to be established by further testing.

The amount of copper sulphate used in the present collectorless flotation tests is about twice that used in conventional flotation. This problem may be resolved by optimizing the reagent balances mentioned above or by finding proper conditions for aerative conditioning, considering that unoxidized pyrite is known to abstract cupric ions (Eq. [6]). The addition of lime during or after conditioning might be used to saturate the pyrite surface with calcium ions and prevent the cupric ion uptake.

Sodium sulphide costs $0.12 a pound (Chemical Marketing Reporter 1977), while thiol-type collectors cost about $0.55 a pound at the present time. Despite the substantial price difference between these two reagents the collectorless flotation using sodium sulphide appears to be a more expensive process than the conventional technique, considering the large amount of the reagent used in the batch type tests. It may be pointed out, however, that as Eq. [2] suggests there are no theoretical reasons to indicate that sulphide ion consumption should be greater than the xanthate ion consumption, unless pyrite abstracts more sulphide ions than xanthate ions, which needs to be proved. If the displacement of surface oxidation products is indeed controlled by well defined, stoichiometric chemical reactions,the sodium sulphide consumption on a pounds-per-ton

basis should actually be less than the alkali xanthate consumption taking into account the differences in their molecular weights. It appears possible, there, that if the mill water of a continuous operation is recirculated, the sodium sulphide consumption could be minimal, perhaps below the level of xanthate consumptiom.

## SUMMARY AND CONCLUSION

1. A method has been devised to recover chalcopyrite from Robert Mine copper ore by flotation without using a collector. The technique consists of wet-grinding the ore using steel balls in the presence of $Na_2S$, which gives chalcopyrite a form of natural floatability while pyrite and other gangue minerals remain hydrophilic. A commercial grade copper concentrate assaying 21.4% Cu has been obtained with a recovery of 68.1% in a batch flotation test. This result is superior to that obtained by using potassium amyl xanthate as a collector in a previous investigation.

2. A copper-zinc ore (Texasgulf Type 'A' ) has been treated successfully by the collectorless flotation technique: chalcopyrite is floated using $Na_2S$, followed by the activation of sphalerite by copper sulphate in the presence of $Na_2S$. Copper concentrates assaying higher than 22% Cu, with over 85% recovery, have been produced by the collectorless flotation. These results are comparable to those of conventional flotation tests conducted by using thiol-type collectors. The best zinc recovery obtained by the collectorless flotation is 77.7%, the concentrate assaying

52.50% Zn. The conventional technique gives a better zinc recovery (80.0%) with the grade of 53.0% Zn.

3. The collectorless flotation of chalcopyrite is best achieved when the pH of the pulp is lowered to about 6 by adding HCl during or after sulphidization; higher grade copper concentrates are obtained but not at the expense of recovery. This has been explained by the depletion of excess $S^{2-}$ and/or $HS^{-}$ ions available for the sulphidization of pyrite at a pH lower than the system point (pH = pKa = 7.1).

4. The collectorless flotation of sphalerite is best achieved when the ore pulp, ground by using steel balls, is subjected to an aerative conditioning with $SO_2$ prior to the copper rougher flotation; the zinc loss in the final copper concentrate is minimized and a higher grade zinc concentrate is produced with improved recovery.

5. Pyrite can be floated from the copper-zinc tailing of a collectorless flotation test at an alkaline pH using potassium amyl xanthate.

6. Potassium permanganate can reactivate sphalerite that has been suppressed, possibly by the excessive use of copper sulphate.

7. The natural floatability of sulphide minerals observed in the present work has been explained as due to the reduction of oxygen on the surface of the clean sulphide mineral, although the possibility of a sulphide mineral possessing inherent hydrophobicity is not denied. Such oxygen reduction could produce a sulphur-rich surface, the excess sulphur being the hydrophobic entity.

8. An ion exchange mechanism has been proposed to account for the removal of oxidation products by sulphide ions, which suggests that sulphidization is controlled by the solubility product of a sulphide mineral. The selective collectorless flotation of chalcopyrite is attributed to its low solubility. The proposed ion-exchange mechanism also suggests that the consumption of sodium sulphide in a collectorless flotation depends on the degree of surface oxidation of the minerals.

9. The activation of sphalerite by cupric ion has been explained by the fact that copper sulphide is less soluble than sphalerite. The activation of pyrrhotite and pyrite appears to be prevented by aerative conditioning.

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